

One-dimensional continuum electronic structure calculations with the density matrix renormalization group

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We extend the density matrix renormalization group to compute exact ground states of continuum many-electron systems in one dimension with long-range interactions. To demonstrate the power of this approach, we find the exact ground state of a chain of 100 strongly correlated artificial hydrogen atoms. We expect this method to be important for simulating 1d cold atom systems and for studying density functional theory (DFT) in an exact setting. Not only can we compare DFT approximations with exact results, but we can implement the exact density functional.

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For electronic structure calculations, these are the best of times and the worst of times. When correlations are weak, density functional theory (DFT) makes it possible to tackle extremely realistic Hamiltonians and large system sizes with reasonable accuracy [1]. For strongly correlated systems, there exist powerful and controllable numerical methods [2] for simulating model lattice Hamiltonians, such as the Hubbard model. However, there are few numerical tools that can treat the combination of strongly correlated electronic systems and realistic microscopic Hamiltonians. In the strongly correlated regime, DFT approximations are neither systematic nor controllable, often leading to unrestrained parameter multiplication and empiricism. Model Hamiltonians rely on the arbitrary truncation of terms that may be crucial in tipping the balance between competing phases. Attempts to bridge the gap between realistic Hamiltonians and strong correlation techniques, such as dynamical mean field theory coupled to DFT, still contain both arbitrary truncations and less than ideal treatment of correlations.

Here we show that at least in the case of one dimension (1d), we can treat both the Hamiltonian and the correlations essentially exactly, even for very large systems. Our approach is based on the density matrix renormalization group (DMRG) [3], the most powerful of the strongly correlated techniques for 1d lattice models. Here we extend DMRG to treat continuum electron systems with long-range interactions. This new approach retains the exponential convergence and near linear scaling with system size of DMRG. As an example, we present a near exact calculation of a system with 100 strongly interacting pseudo-hydrogen atoms.

A key motivation for this method is to study DFT in an exact many-electron setting. For example, we can easily compare various DFT approximations with exact results. Generically, one dimensional systems have strong quantum fluctuations and provide severe challenges for DFT. In addition, we can implement the exact energy functional of the density, the heart of DFT; previously this could only be done for a few electrons. Our DMRG approach also provides new ways to characterize realistic

many-electron quantum systems using quantum information concepts, such as the entanglement entropy across bipartitions of the system. Another motivation for studying this class of systems is that 1d continuum Hamiltonians can be realized exactly in cold atom systems [4, 5].

Presently, real-space DMRG methods for solid-state applications are designed only to work with lattice models. Each site of such a model can be thought of as a Wannier function centered on an atom. One way of generalizing this picture to make the Hamiltonian more realistic is to expand in a set of basis functions; DMRG has become a powerful technique for the quantum chemistry of small molecules based on this idea [6, 7]. Here we proceed in a more flexible direction which does not depend on a choice of basis and has optimal scaling of calculation time with system size: we represent the continuum in 1d with a real space grid. The continuum Hamiltonians of interest can be written as

$$H = \sum_{\sigma} \int_x \psi_{\sigma}^{\dagger}(x) \left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \mu \right] \psi_{\sigma}(x) + \int_x v(x) n(x) + \int_{x,x'} v_{ee}(x-x') n(x) n(x') . \quad (1)$$

where $\psi_{\sigma}^{\dagger}(x)$ creates an electron of spin σ at position x ; v and v_{ee} are local and electron-electron potentials, respectively; and n is the electron density operator. We introduce a grid spacing a , obtaining a discretized Hamiltonian

$$H = \sum_{j,\sigma} \frac{-1}{2a^2} (c_{j\sigma}^{\dagger} c_{j+1\sigma} + c_{j+1\sigma}^{\dagger} c_{j\sigma}) - \tilde{\mu} n_{j\sigma} + \sum_j v^j n_j + \frac{1}{2} \sum_{i,j} v_{ee}^{ij} n_i (n_j - \delta_{ij}) \quad (2)$$

where $\tilde{\mu} = \mu - 1/a^2$, $v^j = v(ja)$ and $v_{ee}^{ij} = v_{ee}(|i-j|a)$. The δ_{ij} in the last term prevents an unphysical self interaction. For technical reasons we work with open boundaries rather than periodic, and extend the grid well past the edge atoms. Finite grid spacing errors can be reduced arbitrarily by reducing a ; convergence can be accelerated

by using a higher order discretized derivative. Here, we fix $a = 0.1$ in atomic units.

A different approach was proposed recently by Verstraete and Cirac [8], who showed how to define and optimize matrix product states directly in the continuum limit in the context of quantum field theories.

Working *efficiently* with such a Hamiltonian represents an unusual challenge for DMRG. Normally, one is most concerned with the number of states per block m needed to represent the ground state. The number of sweeps N_S needed to converge to the ground state is usually quite small ($\sim 2-5$) for 1d systems. Here, the reverse can happen: a small grid spacing ‘ a ’ relative to the interatomic separation can lead to energy scales that differ by orders of magnitude, greatly increasing N_S but not affecting m significantly. Fortunately, while convergence with m reflects the entanglement of the system, an inherent property, many approaches can be tried to reduce N_S . We have found a particularly efficient acceleration approach based on a real-space RG procedure which produces a supplementary grid with a much coarser spacing and lower energy scales such that N_S can be made small; after sweeping on this grid we map the wavefunction back onto the fine grid for further sweeps. This procedure, which will be described in a future publication, introduces no additional approximations; it merely reduces the computational time to reach a converged ground state.

Besides the wide range of energy scales, another challenge for DMRG is the presence of long-ranged interactions. The simplest approach, dealing with N_g^2 terms in a sweep over N_g grid points, would scale as N_g^3 . A more efficient approach using intermediate operators, as used with DMRG for quantum chemistry in a basis set, would scale as N_g^2 . We utilize a much more efficient approach than either of these by using a representation of the Hamiltonian as a matrix product operator (MPO). Finite bond dimension MPOs naturally encode exponentially decaying interactions [9]. Interactions with a power law decay can be approximated to high accuracy by fitting to a sum of N_{MPO} exponentials (usually $N_{\text{MPO}} \leq 15$ is sufficient to obtain an accuracy of 10^{-5}) [10]. Thus the DMRG calculation time is nominally linear in N_g ; specifically, it is proportional to $N_S N_g N_{\text{MPO}} m^3$. Deviations from a purely linear computational effort with the overall system size can come from a dependence of N_S or m with system size; in practice we find that the RG acceleration procedure keeps N_S small. The behavior of m is well-understood for short-ranged model Hamiltonians: for non-critical systems, m is independent of system size. For critical systems, with power-law decaying correlations, m grows only logarithmically with length. Hence, we expect only a slightly worse-than-linear computational effort with system size in the worst case.

As a simple setting for exploring strong many-body correlation effects, we consider chains of one dimensional ‘soft hydrogen’ atoms. Each atom is modeled as a single

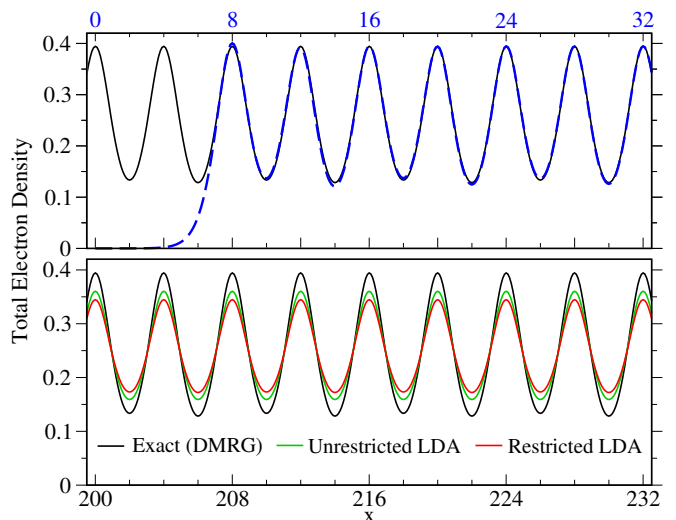


FIG. 1. The exact ground state density of a chain of 100 widely separated artificial atoms. The total length of the system is $L = 420$ in atomic units (4200 grid sites with a spacing of 0.1). The upper panel shows the electron density of a central region superimposed with the density at the left edge (the dashed blue curve with corresponding x axis at the top of the plot). The lower panel shows the electron density predicted by DFT within the local density approximation, for both restricted and unrestricted spin densities.

electron in a soft-Coulomb potential well of the form

$$v_{\text{atom}}(x) = -1/\sqrt{x^2 + 1}, \quad (3)$$

where we use atomic units throughout. We also include repulsive interactions defined by $v_{ee}(x - x') = -v_{\text{atom}}(|x - x'|)$. This potential is a standard choice for avoiding complications arising from divergent Coulomb interactions and has been used to study molecules in intense laser fields [11, 12]. We are also fortunate to benefit from the work of Ref. 13, which provides a parameterization of the 1d local density approximation (LDA) for just such an interaction.

As a demonstration of the power of our approach, we display in Fig. 1 the exact ground state density of a chain of one hundred artificial atoms with long-range interactions, which took a few days of computer time on a single workstation. Representing the ground state accurately required keeping about $m = 200$ states. The energy error in the many-body solution using DMRG is of order 10^{-4} . The errors arising from the finite grid spacing and finite number of exponentials N_{MPO} used to fit v_{ee} are larger, of order 10^{-2} , but are well understood and easily reduced if necessary. Also shown are both restricted and unrestricted DFT calculations using the 1d LDA [13]. In this system both DFT approaches have substantial errors. In terms of lattice models, one would represent such a system with either a half-filled Hubbard chain or with an antiferromagnetic Heisenberg chain. Note that both of these models are critical with power law decaying spin-spin correlations; a non-critical system would have

been easier for DMRG. It is not surprising that the local DFT methods cannot capture the quasi long-range order quantitatively, with the unrestricted LDA giving long-range antiferromagnetism (similar to Fig. 2). It is somewhat surprising that even the total density from DFT deviates strongly from the exact DMRG results. The total energy from either DFT calculation is off by about 1%.

In Fig. 2 we show a system which reveals weaknesses of both DFT and of model Hamiltonian approaches. The figure shows the exact ground state density of ten atoms with interatomic spacing $b = 4$. The edges induce a staggered pattern of strong and weak bonds which decays slowly into the bulk, and is therefore significant throughout this small system. Qualitatively, we can understand the staggered behavior from a 10 site Hubbard model (at half filling with $U/t = 4$ chosen arbitrarily) or a 10 site Heisenberg model. The Heisenberg ground

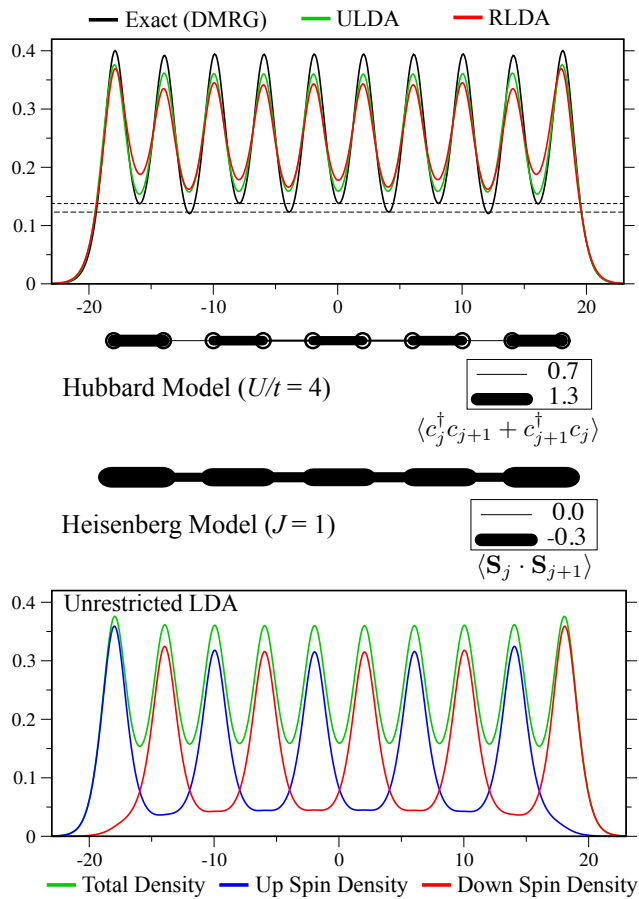


FIG. 2. Spontaneous dimerization of the density for a chain of 10 soft hydrogen atoms with interatomic spacing $b = 4$ (dashed lines are a guide to the eye). The upper panel compares the densities predicted by DFT within the LDA approximation; the lower panel shows the spin densities for the unrestricted LDA. Also shown is the expectation value of the kinetic energy for a Hubbard model and the exchange energy for the Heisenberg model on 10 lattice sites.

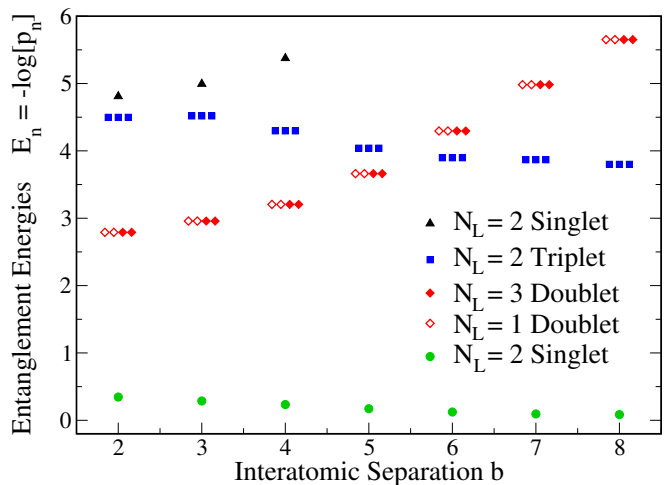


FIG. 3. Entanglement spectrum at the center of interacting 4-atom chains with various interatomic separations b . N_L refers to the number of electrons to the left of the cut for each density matrix eigenstate.

state has resonating valence bond character; in a perfect near-neighbor RVB state, the edges would suppress all resonance and drive the weak bonds to zero. The actual Heisenberg ground state has longer range resonances which reduce these effects. In the Hubbard model, the strong exchange bonds show up as bonds with lower kinetic energy. However, neither lattice model reveals the increased electron density on the strong bonds, stemming from the strong hopping. The exact results suggest that these models might be improved by bond-dependent interactions t and J . The DFT calculations capture even fewer properties of the true ground state. Unrestricted LDA predicts an energy $E_{\text{ULDA}} = -11.364$ which is close to the exact energy $E_0 = -11.496$, but it predicts no staggered bond density and breaks spin symmetry, producing a long-ranged antiferromagnetic state as shown in the lower panel of Fig. 2. Restricted LDA captures the staggered density pattern qualitatively, but gives a slightly higher energy $E_{\text{RLDA}} = -11.323$ and fails to reproduce the correct local spin correlations since its wavefunction is a Slater determinant of extended orbitals.

The onset of strong correlation with increasing bond length is often identified with the Coulson-Fischer point [14], where an unrestricted Hartree-Fock calculation spontaneously breaks spin symmetry. A different way to distinguish strong from weak correlation is by examining the entanglement spectrum, readily accessible in DMRG. Defining the left reduced density matrix $\rho_L = \text{Tr}_R|\Psi\rangle\langle\Psi|$, where the trace is over all grid points in the right half of the system, the entanglement spectrum consists of the energies of the entanglement Hamiltonian $H_E = -\ln \rho_L$ [15]. The most probable density matrix eigenstates are those in the low ‘energy’ part of the entanglement spectrum. By classifying these states according to their total

particle number N_L , we can understand the dominant quantum fluctuations of the ground state. Figure 3 shows the entanglement spectrum at the center of a series of four-atom chains with increasing interatomic separation. A sharp crossover at $b \simeq 6$, where the probability for charge fluctuations drops below that of pure spin fluctuations, signals the onset of strongly correlated behavior.

The foundation of DFT is the Hohenberg-Kohn theorem, which states that for a specific type of interaction and a ground state electron density $n(x)$, the potential $v(x)$ giving this density is unique if it exists [16]. This implies that the total energy and various terms such as the kinetic energy are functionals of the density. Standard DFT approaches are based on approximate functionals where the approximations are explicit formulas. However, having an exact many-body Schrodinger equation solver make it possible to implement the functionals exactly, not as formulas, but as algorithms. The key step in each algorithm is performing an inversion, an iterative calculation of the potential which gives rise to a specified density. (Note that an interacting inversion is much more difficult than the non-interacting inversion needed to compute the Kohn-Sham potential from the exact ground state density [17, 18].) Interacting inversions have previously been done only for a 1d two-electron system during a time evolution [12]. To demonstrate that we can perform interacting inversions of any reasonable density (we exclude densities that vary appreciably on the grid scale, for instance), Fig. 4 shows an interacting inversion of the density $\tilde{n}(x) = e^{x/15 - x^2/2 + x^4/20 - x^6/750}$ normalized to contain four electrons. We begin with a

trial potential $\tilde{v}(x)$ from which we obtain the trial density $\tilde{n}(x)$ using DMRG. Then the potential is updated as $\tilde{v}(x) \rightarrow \tilde{v}(x) + \alpha(\tilde{n}(x) - n(x))$ for some $\alpha > 0$. This procedure can be motivated heuristically or from a minimization principle. By taking $\alpha = 0.5$, the inversion in Fig. 4 converged in 300 steps such that the maximum difference between the inverted and target densities was less than 0.01. Once an inversion is done, it is simple to obtain exact density functionals, such as the ground state energy $E_0[n]$, because one has obtained the many-body wavefunction.

Many oxide materials of current interest are too strongly correlated for present DFT methods, but crucial properties must be calculated to an accuracy far beyond that of simple model Hamiltonians. The method described here provides a new, alternative route to studying strongly correlated systems. All existing approximations, from heuristic corrections to standard functionals, such as LDA+U [19], to methods developed for lattice models, such as dynamical mean field theory [20], can be applied and tested more easily, thoroughly, and accurately in the present setting. Because our 1d world captures a feature crucial to density functional approximations, namely the continuum instead of a lattice, such studies should provide the insight needed to construct more accurate density functionals for real strongly-correlated materials.

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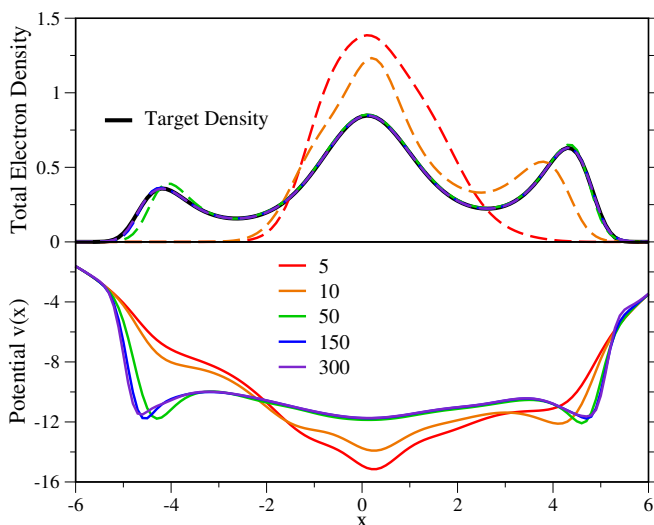


FIG. 4. Interacting inversion of an artificial density for a four electron system, labeled here as the target density. The lower plot shows trial potentials at 5 selected steps. The dashed curves in the upper plot are the corresponding trial densities found by computing the ground state in each potential with interactions given by $v_{ee}(x) = 1/\sqrt{x^2 + 1}$.

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